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THE ELECTRODEPOSITION OF ZINC ON ZINC STARTING SHEETS[1] [2]

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ABSTRACT

The conditions necessary for making thick electrodeposits of zinc on zinc starting sheets were investigated with the object of eliminating the stripping costs and reducing melting losses, which occur under the present practice of using aluminum starting sheets. Finished cathodes as thick as 2.6 inches (6.6 cm) were produced on sheets rolled from four-nines zinc, and cathodes as thick as 1 inch (2.5 cm) were produced on sheets of commercial grade zinc. These results were obtained by rigorous purification of cell feed solution and by using cathodes of special design. Compared to present aluminum starting sheet costs, the use of zinc starting sheets is expected to offset in part, if not completely, the expense of the extra liquor purification step. This would leave intact the savings effected by eliminating the zinc stripping step and by reducing melting losses.

INTRODUCTION

Since the establishment of the electrowinning of zinc on a commercial basis about 1916, aluminum sheet has been used as the cathode material. Earlier attempts to adapt zinc sheet to this purpose were not successful, owing to the tendency of the zinc to redissolve in the electrolyte in the cells, particularly at the level of the solution, and contacts between starting sheets and support bars have not been satisfactory (1). The use of aluminum cathodes in electrolytic zinc cells is thoroughly established as a commercially feasible practice, a fact that has lessened the incentive to study zinc cathodes for this purpose despite some obvious savings if zinc could be used successfully.

When aluminum cathodes are used, certain maintenance costs are entailed in replacing the cathodes that have become worn and corroded. Another charge must be made for strips to protect the edges of the sheet so that the zinc deposit can be readily stripped from the aluminum. Eliminating the cost of stripping the deposit is the most important economy that would result if zinc starting sheets were used for the electrolytic deposition of zinc. Zinc stripped from aluminum cathodes is obtained in thin sheets which are melted only with dross losses of $2\frac{1}{2}$ to 4 per cent. Dross loss possibly could be reduced to $\frac{1}{2}$ per cent or less if zinc starting sheets could be successfully operated for residence periods three or four times that currently used in electrolytic zinc plants.

These possibilities of saving in the cost of stripping and melting have maintained at least some interest in zinc starting sheets and in longer residence periods of the cathodes in the cells. Although there are few literature references to the work, many attempts have been made to electro-

[1] Manuscript received March 29, 1949. This paper prepared for delivery before the Philadelphia Meeting, May 4 to 7, 1949.
[2] Not subject to copyright.

deposit zinc on zinc starting sheets. Conversations with the personnel of electrolytic zinc plants reveal that a certain amount of work was done on these problems early in the development of the present electrolytic processes, and at least one company is now actively engaged in such a study. O. C. Ralston, Chief of the Metallurgical Division of the Federal Bureau of Mines, met with considerable success in developing thick deposits of electrolytic zinc. In order to mitigate the effects of solution-level corrosion, he progressively lowered the level of the electrolyte in the cell. He thereby exposed thicker sections of deposited zinc in the region of most rapid corrosion (2). Starting sheets were zinc stripped from aluminum cathodes. He also employed protective coatings, pervious to zinc ions, applied to the edges of the sheet to prevent treeing (3). Attempts to use rolled sheet instead of stripped electrolytic sheet have met with greater discouragement, owing to the impurities which normally accrete during the melting and rolling operations.

MATERIALS AND EQUIPMENT

The source of zinc for all of the experimental work was a calcined zinc concentrate obtained from the electrolytic zinc plant of the Sullivan Mining Company at Kellogg, Idaho. Two different shipments were obtained with no essential differences in composition. Changing from one lot to the other had no adverse effect on the quality of the zinc deposited. The analysis of the first lot is given here in detail and that of the second lot for only major constituents. The minor constituents were assumed to be essentially the same as in the first lot.

Analysis in per cent, lot 1: Zn 56.6, Pb 4.5, Fe 7.7, Si 1.5, Cu 0.25, Co 0.015, Ni less than 0.005, S (total) 3.2, SO_4 7.6, Cd 0.26, Sb 0.001, As 0.02, Mn 0.19, Se less than 0.005, Te less than 0.005, Au trace, and Cl trace. The spectrograph showed Sn, Ge, Tl, Bi, and In to be nil. Silver was present amounting to 4.5 ounces per ton. Lot 2 analyzed Zn 57.2, Pb 4.5, Cu 0.3, Fe 7.7, S (total) 2.8 per cent, respectively, and silver 4.8 ounces per ton.

Mechanically agitated batch-leach equipment was used. The scale progressed from beakers, to 20-liter glass jars, to 55-gallon (208 l) steel drums. The method of heating progressed from hotplates, to electrically-heated water baths, to copper-sheathed bayonet-type electric heaters, in the case of the steel drums. Vacuum filtration was employed because of its availability and not by virtue of any superiority over pressure filtration. Buchner funnels were used in the earlier experiments, but Moore-type filter leaves were used when the leaching was done in the large drums.

Copper oxide rectifiers were used to supply the direct current and, since the cells were operated singly, a chromel resistance was put in series with each cell to raise the resistance of the circuit high enough to stabilize the operation of the rectifiers.

The deposition cells were rectangular, glass aquaria 14 cm wide, 25 cm long, and 15 cm deep. A hole 1 cm in diameter was drilled about 1 cm from the top of each cell on one end. A gooseneck siphon was inserted through this hole and fitted tightly, to provide an intermittent discharge of the spent electrolyte. Fig. 1 shows a cell in operation. The cells usually were operated with two anodes and one cathode, but as many as three cathodes

and four anodes were employed at one time. The anodes were connected directly to the anode bus bar. The cathodes were connected to the line through ammeters. Each cathode had its own ammeter so that the current efficiency could be calculated. One cell was always operated in the line with an integrating ampere-hour meter. This instrument was calibrated by a copper coulometer. The anode spacing was 5 cm in the case of the three cathode cells. It was not critical in the single cathode cells. When the

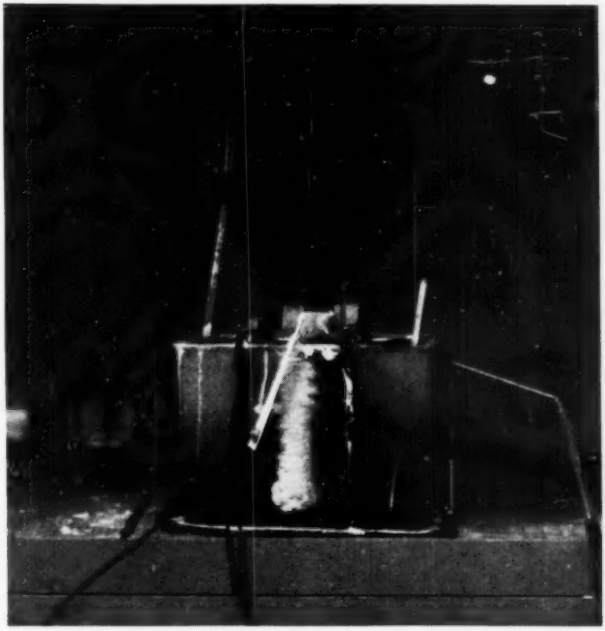

FIG. 1. Electrolytic cell in operation on the eighteenth day, with the cathode 1 inch (2.54 cm) thick.

cathodes were operated for long periods, it was necessary to increase the anode spacing from time to time in order to preserve the proper distance between the anodes and the cathode.

The anodes were of 2.5 cm-grid-construction cast from a lead alloy containing 1 per cent silver. The alloy was obtained from the same company as the zinc concentrate and was cast in our foundry. They were supported by the side walls of the cell and, in turn, supported the copper anode bar.

Several kinds of cathodes were used, including cathodes of aluminum, locally rolled zinc, commercially rolled zinc, and electrolytic zinc stripped from aluminum cathodes. The aluminum cathodes were used for the earlier experimentation for all deposition tests. Later, they were used to supply

daily test samples by being operated in the 3-cathode cell along with other cathodes. They were stripped each day and returned to the cell. The stripped electrolytic sheet was used for the first zinc starting sheets and presented no serious problem in the size of cell employed in this study. They will be considered again when cathodes of commercial size are operated.

The sheet rolled at this laboratory was fabricated from our own electrolytic zinc, first melted, then cast into pigs. The pigs were scalped to remove the scale from the top surface and rolled at a temperature of about 150 C to a thickness of about 0.03 inch (0.076 cm). Several thicknesses of commercially rolled zinc ranging from 0.005 to 0.05 inch (0.127 cm) were used. This zinc contained 0.13 per cent lead along with small amounts of

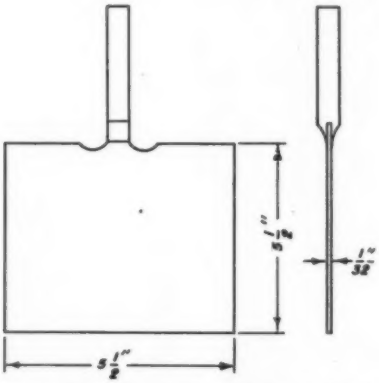

FIG. 2. Flat and edge view of a zinc starting sheet

other impurities, including copper, nickel, and cobalt, thereby making it significantly lower in grade than our own product.

After experiments with a few designs of cathodes, including a sheet of zinc held by an aluminum clamp and one in which the sheet was held by two zinc hangers, one gripped to each top corner, a single suspension type was adopted. Fig. 2 shows the essential features of this design. The starting sheet consists of two parts; the sheet cut from rolled or stripped-zinc, and the hanger cut from thicker rolled zinc. The hanger blank was shaped, notched to receive the sheet, and then attached to the sheet by pressure. In the case of sheets of commercial size, other means of attachment such as zinc rivets, spot welding, or electric welding may be required. All of these methods were successfully used but were not required in laboratory practice. After a tight joint had been formed, it was dressed with a sanding wheel so that there was a smooth articulation of the sheet with the hanger. A slight taper below the upper end of the hanger made a tight wedge fit in a slot in an aluminum conductor bar. This joint served well as an electrode support and electrical contact.

PROCEDURE

Zinc was brought into solution by leaching the roasted zinc concentrate with spent acid from the cells. Electrical heating was employed to supplement the heat of reaction so that the leach temperature remained above 80 C. The agitation was continued for 4 hours or longer at this temperature. The slurry was filtered hot, and the filtrate was returned to a heated vessel for treatment with zinc dust. It was treated four times, using 2 grams of zinc dust per liter in each treatment, making a total of 8 grams of zinc dust per liter. It is quite likely that this treatment was more rigorous than was necessary, but it prevented the zinc-purification operation from being a variable in the electrolytic precipitation step.

The hot filtrate from the fourth zinc-dust treatment was reheated to 80 C and treated with potassium permanganate crystals until the clear solution remaining, when the precipitate settled, was faintly pink. The precipitate was filtered off. The purified liquor was stored until a laboratory analysis was obtained and a trial run was made in an electrolytic cell. A typical analysis of the purified solution, which contained 150 grams per liter of zinc, was Ni 0.05, Co 0.05, Cu 0.06, Cd 0.4, Fe 0.5, Mn 5.0, Pb 0.6, and Sb 0.003 milligram per liter. If the cell test proved satisfactory, the liquor was used to prepare cell feed; if not, it was retreated as the test results might indicate.

The feed solution for the cells was made from the purified leach liquor by adding water and sulfuric acid to bring its composition to 100 grams of zinc and 37.5 grams of acid per liter. This method insured the preparation of a solution with uniform physical properties from leach liquor when the zinc content varied from leach to leach. Uniform specific gravity and viscosity were essential to the proper regulation of the feed rate; and, for this reason, the feed solution was carefully prepared. It was placed in a glass bottle on a shelf above the cell. This bottle was connected by a siphon to a small bottle which maintained a constant level by admitting air to the supply bottle when the level in the small bottle had fallen below the air inlet. This permitted the siphon to flow until the air inlet was covered. Another siphon from the constant level bottle fed the cell through a capillary tube for which the length and bore were carefully adjusted to maintain the desired flow rate.

The cell was put in operation by filling it with a solution containing 50 grams of zinc and 112 grams of acid per liter, which is approximately the composition of electrolyte in the commercial low current density cells. The electrodes were set in place, and the electric current supply was connected. The current density was brought up to about 35 amperes per square foot (3.8 amp/sq dm); the solution feed rate was adjusted so that it supplied zinc to the cell at the rate it was deposited and there was no essential change in the composition of the electrolyte. Each day the cathodes were removed, rinsed, drained, and weighed. A sample of the electrolyte was taken for analysis, and an aluminum cathode was stripped to supply a sample of the deposit in the case of the three-cathode cells. The current efficiency was computed from the change in weight of the cathode and the change in the ampere-hour reading. If the current efficiency or the appearance of the cathode indicated inferior feed solution, the feed

was shut off until the supply bottle could be emptied and refilled with new solution. If this expedient did not restore the current efficiency to 90 per cent or above, the cathode was considered to have failed.

Several methods of treating the starting sheets before putting them into service were tried without marked success. Aluminum was benefited by being pickled in dilute sulfuric acid; but, obviously, this treatment was not applicable to zinc. Although it was possible to start a zinc sheet without removing a heavy oil film, it was found that preliminary cleaning would result in a smoother deposit. A wash in caustic soda or sodium carbonate solution was effective for this purpose. A mercury strike offered little encouragement. A preliminary gassing in a cell containing only acid in the electrolyte gave the best results of all cleaning treatments tried, but no treatment at all was finally adopted as standard practice. The normal gassing of the cathodes during cell operation was sufficient to clear them of the adhering bubbles.

The cells were operated with the electrolyte temperature at about 29 C. A few tests were made with auxiliary heat applied to bring the temperature to 40 C. These tests were neither rigorous nor complete enough to show any effect of temperature over this range. It has been necessary to operate the cells without supervision overnight. This led to operation under various unfavorable conditions, such as power failures, blocked feed lines, and changes in temperature with consequent changes in flow rate of the feed solution. None of these adverse conditions resulted in failure, if they occurred for a brief period when the cathode was operating at high efficiency, but the danger increased as the current efficiency became less. A slow feed rate or a blocked feed line leads to a high acidity in the cell. A high acidity appears to be advantageous at the beginning of the residence period, owing to the smoother deposit which results, but the opposite is true a few days later. This observation led to the conclusion that a cathode fails because of all the adverse factors to which it is subjected, and it is virtually impossible to evaluate properly the effect of any one factor independently.

The problem of excess growth of the cathode at the edges has been troublesome because recesses develop at the junction of this rim with the sheet. The recesses are not supplied with sufficient current to prevent corrosion in the electrolyte. In single cathode cells, the distribution of current over the cathode can not be effectively controlled by the size of the anode, and the residence period is definitely shortened by excess growth at the edges. One cathode which failed at 14 days was freed of its excess edge growth and was returned to the cell for another 14 days of operation. This effect is markedly reduced by using three cathodes. Edge growth has been controlled within the required limits by baffles which screened the edges of the cathode from the path of the current. After a few days of edge protection, the cathode was thick enough that the increased amount of surface at the edges compensated for the excess current in the adjacent regions and continued protection by baffles was not required.

DISCUSSION

Of the factors that limit the residence period of cathodes, the purity of the feed solution seemed to be most important. Composition changes, which were not detected in routine analytical procedures, apparently caused noticeable changes in the electrolytic deposit. Comparison of a

large number of deposits showed no two to be so nearly alike as to be indistinguishable. The effects of certain impurities are known, notably of nickel, cobalt, and antimony. As these were more completely removed, the electrolytic deposition improved, but other effects began to appear, the causes of which were not known. Rather than attempt to unravel the tangle of these unknown causes, it was deemed advisable to study the problem from the standpoint of the methods of treating the crude leach liquor.

The conventional treatment with zinc dust produced a solution that gave conventional results in the electrolytic cell. Further treatment with potassium permanganate yielded a solution of higher purity, and this combination of treatments, properly performed, produced a purified liquor from which has been deposited cathodes as thick as 2.6 inches (6.7 cm) after a residence period of 39 days. Table I gives the current-efficiency record of this deposit. If a preliminary test showed that the treating procedures were inferior, the permanganate treatment was repeated by first adding a small amount of manganous sulfate to the solution before a second addition of permanganate. The permanganate treatment was particularly effective in removing cobalt, manganese, antimony, and iron.

Laboratory and larger-scale tests indicated that the amount of permanganate required agreed closely with the value calculated from the amount of oxidizable impurities in the solution. Divalent manganese made the heaviest demand with divalent iron second. The demands of cobalt and antimony were negligible in comparison with the first two. An excess of 10 to 15 per cent over the needs for manganese and iron sufficed to meet all other demands including organic debris. The heaviest requirement encountered was 8.6 pounds (3.9 kg) permanganate per ton of zinc. Depending on the market price of permanganate, the cost of this treatment would range from $1.75 to $2.50 per ton of metal produced. The precipitated oxides of manganese are obtained in a filter cake relatively free from other material, so that they would be easy to process for reuse. Economies which may be expected from reuse of the precipitate could be considerable, so the cost of this step might be less than $1.00 per ton.

The purity of the starting sheet material was second in importance as a factor which determined whether a cathode would continue for an extended period in a cell. Once the starting sheet is covered with an electrolytic deposit, it should attain a uniformity permitting it to operate until the recesses, which develop with age, lead to excessive resolution. Actually, the electrodeposited zinc is never free from pinholes and always has points with a low enough hydrogen overvoltage to collect bubbles of hydrogen which screen the point in question from electrolytic action. In this work, the higher the purity of the zinc in the starting sheet, the less likely were the bubbles to persist and the more likely was the void, kept open by the bubble, to be eventually covered over with zinc. In Fig. 3, No. 5 is a cross section through a 28-day deposit which shows the healing phenomenon. The pits which outline the starting sheet in the center give way to sound dense metal a short distance out.

In the case of less pure sheet, a greater number of pinholes developed, and local action set in early to enlarge them so that the entire starting sheet was sometimes corroded away, leaving the deposit more or less intact around the void. Fig. 4 shows this condition. It resulted when the deposit became so thick that the remote regions of the pits were no longer

protected by the current, and corrosion of the starting sheet set in. High purity of the electrolyte was effective in combatting this type of cathode deterioration, and preliminary gassing of the cathode in dilute acid offered

TABLE I. *Current efficiency record of a 39-day deposit of zinc on a rolled-zinc starting sheet*‡

Day	Weight grams	Current efficiency	Remarks
0	145	—	Weight of starting sheet.
1	465	95.4	Deposition proceeding normally.
2	709	95.2	Do.
3	989	92.3	Do.
4	1143	89.8	Feed solution changed.
5	1438	97.0	Deposition proceeding normally.
6	—	—	Sunday—cell not attended.
7	1951	92.8	Deposition proceeding normally.
8	2213	91.0	Do.
9	2454	90.4	Do.
10	2733	94.0	Do.
11	3006	93.5	Do.
12	3306	90.6	Do.
13	—	—	Sunday—cell not attended.
14	3799	89.0	Deposition proceeding normally.
15	4070	92.0	Do.
16	4332	86.5	Do.
17	4583	84.8	Anode spacing increased.
18	4838	82.3	Deposition proceeding normally.
19	5081	73.3	Feed solution changed.*
20	5420	94.2	Return to previous solution.
21	5599	88.7	Feed solution changed.
22	5861	91.6	Deposition proceeding normally.
23	6116	93.4	Do.
24	6369	90.7	Do.
25	6633	93.2	Do.
26	6883	93.8	Do.
27	7194	88.7	Feed solution changed.
28	7426	91.8	Deposition proceeding normally.
29	7840	91.4	Do.
30	8097	92.3	Do.
31	8355	89.0	Do.
32	8616	88.8	Do.
33	8892	88.3	Do.
34	9150	83.5	Do.
35	9397	87.0	Do.
36	9645	88.7	High acidity corrected.
37	9805	93.7	Deposition proceeding normally.
38	10038	79.6	Feed line plugged overnight.
39	10282	83.4	Deposition terminated.
	10110		Dry weight.

* Feed line plugged overnight.

‡ Total ampere-hours by the meter, 9241; theoretical weight at 100 per cent current efficiency, 11262 g; over-all current efficiency, 89.8.

some promise. The real solution seemed to be to produce rolled sheet of higher purity. This does not present any serious technical difficulties and probably would facilitate fabrication of the cathodes.

Cathode operation was also given serious consideration along with

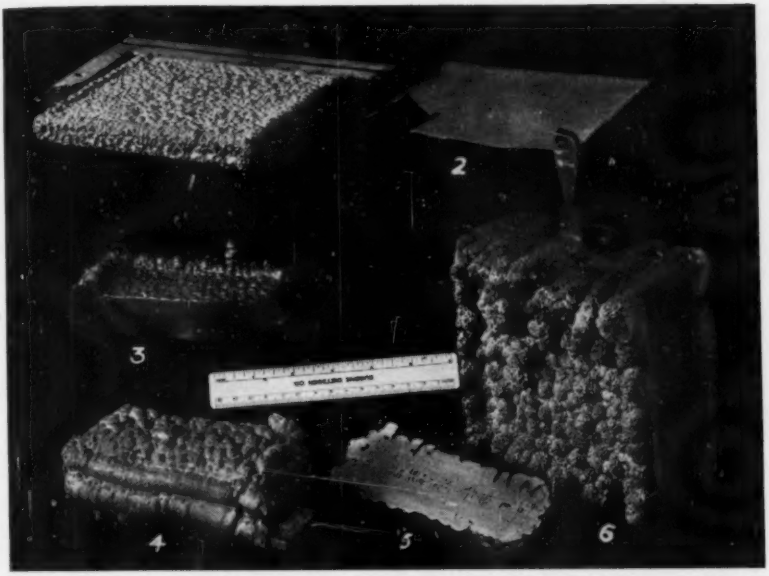

FIG. 3. Samples of electrodeposited zinc. 1. 8-day deposit on aluminum cathode; 2. 1-day deposit on aluminum cathode; 3. 18-day deposit on zinc starting sheet; 4. 28-day deposit on zinc starting sheet; 5. section through the 28-day deposit; 6. 39-day deposit on zinc starting sheet. Over-all current efficiency, 89.8%.

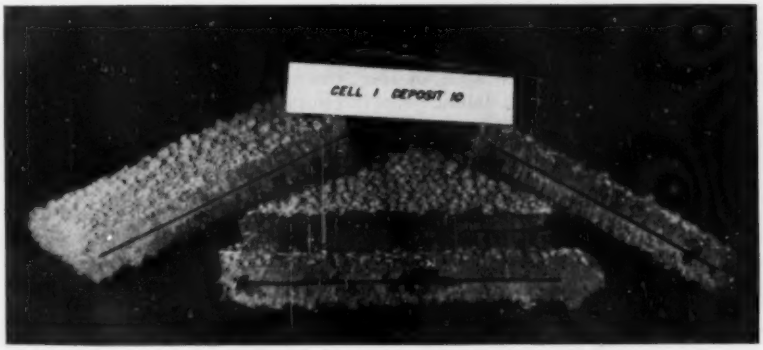

FIG. 4. Section through a cathode showing corrosion of the starting sheet

design in connection with the problem of solution-level corrosion. The starting sheet was suspended entirely below the surface of the electrolyte so as not to be subject to solution-level corrosion. The second, thicker section of rolled zinc, which gripped the center of the top edge of the sheet

and supported it in position, had a greater cross section in the region of the level of the solution and successfully resisted attack. As the electrodeposit accumulated, it covered the junction of the two parts of the cathode, so that the mechanical strength of the joint increased with the weight it was called upon to support. The hanger was carefully beveled in the region of the joint. When this beveled section was held in such a position that the fluctuating solution level moved up over it and then fell, the joint was built up so that it articulated smoothly with the sheet leaving no projections which would later contribute to the failure of the cathode. Fig. 3, No. 6, shows this type of union in which the joint between the hanger and the sheet is recessed in a notch, so that the top of the cathode was above the solution level when the level was low. This helped control excess growth along the top edge.

Cathode failure was defined earlier as the failure of the cell to operate at a high current efficiency, which, in this work, ranged as high as 95.5 per cent. The general tendency was for the efficiency to drop slowly from day to day even under the best of conditions. If a sudden drop occurred, an attempt usually was made to correct it by changing to a new feed solution. In most cases, a purer feed solution improved the efficiency more or less permanently if the cathode still retained its initial sound surface; but, if the surface was nodular or pitted, only transient benefit resulted.

Usually, the causes of failure could be recognized and, if impurities were suspected, they could be promptly eliminated by supplying new solution. Certain other types of failure were not amenable to this treatment. When the hanger and the starting sheet were both made of soft zinc rolled at the Albany Station, no serious corrosion developed at the joint, but when a soft-zinc hanger was used to hold a sheet made of the harder commercial zinc, the lack of uniformity between the two was sufficient to induce corrosion that was difficult to combat. At present, this problem seems to have been solved by careful adjustment of the position of the joint with respect to the solution level at the beginning of the deposition period. If this joint receives, initially, a sound deposit over the area of contact between the dissimilar samples of zinc, the nonuniformity is corrected by the electrodeposit before damage can develop. Under this practice, separation of the hanger from the sheet has become a relatively minor cause of failure.

The edges of the cathode are subject to a higher current density than the flat areas. The result is that, when the cathode is thin, the growth is more rapid at the edges. Baffles were arranged so that they screened the edges of the starting sheets. Properly designed and placed, these baffles completely controlled excess growth along the sides of the cathode. This type of control is capable of being incorporated into the design of the cell by making the baffles a part of the cell wall. Further relief from this edge effect is expected when the number of cathodes in the cell is increased. This prevents the current conducted by the end zones outside the anodes from contributing current to the solution at the edges of the cathode. As a consequence, a smaller anode could be utilized to decrease the current density at the edge. In addition to this, an increase in the size of the cathode from laboratory scale to plant scale will reduce the ratio of the area of cross section of the conducting solution to the area of the cathode.

The solution purification required for long residence periods is sufficient to insure the deposition of four-nines zinc with the exception of lead, which enters the electrolyte by dissolution from the anodes. Manganese in the cell feed has been proved to reduce this dissolution and, consequently, a test was made to determine its effect quantitatively. The results are shown in Table II. The average lead content of 13 cathodes from cells using aged anodes was 0.0016 per cent.

While these results indicate the effect usually attributed to manganese in reducing the lead content of the cathode, the quantitative relationship is not consistent with results obtained with aged anodes where less manganese was present in the electrolyte. The aging of the anodes, according to this observation, is of greater importance than the amount of manganese in the cell electrolyte.

Starting sheets may be fabricated from zinc sheet stripped from an aluminum cathode or from sheet rolled from cast zinc. Both types were used successfully. The advantages which accrue to stripped sheet seem to be due to its higher purity, whereas rolled sheet has the advantage of uniform thickness, smooth surface, and less tendency to warp. In commercial plant

TABLE II. *Amount of lead found in zinc cathodes as a function of the manganese in the electrolyte*

Cathode No.	Manganese in electrolyte, mg/l	Lead in cathode, per cent
1	10	0.0038
2	20	0.0037
3	30	0.0032
4	40	0.0031

operation, possibly the required handling would tend to contaminate the stripped sheet and, also, introduce strained places by bending. It would thus lose some of its advantage of purity. On the other hand, considerable care is required to preserve the initial purity of the metal while it is being melted, cast into pigs, and rolled into sheets.

The results obtained, up to the present, indicate that either form can be used successfully as starting sheets for prolonged residence periods to produce cathodes an inch (2.54 cm) thick when the operating conditions are suitable.

The cost of fabricating zinc starting sheets can not be estimated from present information; but, since the starting sheet is only 3 to 5 per cent of the finished cathode, only a small cost will be reflected in the final product. It is believed that this will be less than the cost of losses and maintenance, in the case of aluminum sheets. It is possible that the amount saved will cover the major portion of the cost of the permanganate purification step.

CONCLUSION

With sufficiently pure solutions, thick electrodeposits of zinc can be produced on zinc starting sheets. The purity of the starting-sheet metal is second in importance only to solution purity. The cost of zinc starting sheets will be less per pound of zinc produced than the maintenance on

aluminum starting sheets. This saving may offset the cost of permanganate treatment to purify the cell feed. An important saving in stripping costs and in the dross losses in melting can be made by using zinc starting sheets instead of aluminum.

ACKNOWLEDGMENT

The experimental work at the Albany Station of the Federal Bureau of Mines was proposed by O. C. Ralston in 1945 and has followed his earlier developments.

Any discussion of this paper will appear in the discussion section of Volume 96 of the TRANSACTIONS of the Society.

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EXPERIMENTS IN CHROMIUM ELECTRODEPOSITION WITH RADIOACTIVE CHROMIUM[1]

FIELDING OGBURN AND ABNER BRENNER
National Bureau of Standards, Washington, D.C.

ABSTRACT

Any chromic acid electroplating bath that has been used contains some trivalent chromium. Whether the metal is deposited from this bath directly from the hexavalent state or through the trivalent state has never been conclusively demonstrated.

By tagging the chromium in either of the two valence states with a radioactive isotope of chromium, the radioactivity of the deposit should indicate from which valence state the metal is deposited. Such experiments show that the chromium is deposited directly from the hexavalent chromium and not from the trivalent chromium present in the bath.

INTRODUCTION

The electrodeposition of chromium from the chromic acid bath was first reported by A. Geuther (1) in 1856. Since then, this bath has come into very wide commercial use, and is, at present, practically the only chromium plating bath that is used commercially. The composition of this bath and the mechanism of the electrodeposition of chromium from it have been extensively studied by numerous investigators, but there is no general agreement among the different theories proposed.

Kasper (2) and Snavely (3) have reviewed the theories of chromium plating. These theories may be divided into two groups: (*a*) those that involve direct reduction of the hexavalent chromium to chromium metal, and (*b*) those that involve a stepwise reduction through the trivalent and divalent states. The direct reduction theory is strongly supported by the work of Kasper (2) who showed that even when relatively large amounts of zinc, nickel, cadmium, iron, or copper salts were added to a chromic acid bath, these metals could not be deposited. Therefore it would not be expected that trivalent chromium, which is more difficult to deposit than these metals, would be deposited in the presence of chromic acid.

When radioactive chromium is used to tag either the hexavalent or trivalent chromium in a chromic acid bath, the presence or absence of the tagged chromium in a deposit from that bath indicates the source of that chromium. It has been demonstrated by this method that chromium is deposited directly from the hexavalent state. This would be difficult to prove by any other method.

RADIOACTIVE CHROMIUM

The tracer used in these experiments was Cr^{51}, which is a soft gamma ray emitter with a half-life of 26.5 days. This isotope was obtained from Oak Ridge National Laboratory as small pellets of chromium metal which con-

[1] Manuscript received July 25, 1949. This paper prepared for delivery before the Chicago Meeting, October 12 to 15, 1949.

tained a minute quantity of the Cr^{51}. This preparation will be referred to as the "tracer" in this paper.

Weighed portions of the metal were dissolved in dilute hydrochloric acid, the solution was evaporated to dryness to remove excess acid, and the residue was taken up in water. The resulting solution of chromic chloride was used as the source of active trivalent chromium.

Active hexavalent chromium was prepared by adding hydrogen peroxide with either ammonium hydroxide or sodium hydroxide to a portion of the solution of active trivalent chromium and heating the mixture on a steam bath. When all the chromium had been oxidized to chromate, the solution was evaporated to dryness to remove excess ammonium hydroxide and hydrogen peroxide. The residue was then taken up in water.

To measure the radioactivity of the solutions and deposits, a thin-walled glass gamma ray counter was used in conjunction with a scaler. The solution was placed in a test tube alongside the counter. The deposit from the chromium bath was made on a brass cylinder, within which the counter was subsequently placed.

ISOTOPIC EXCHANGE

It is known that isotopic exchange frequently occurs between different valence states of the same metal. Therefore it was necessary to determine the extent to which isotopic exchange takes place between trivalent chromium and chromic acid in the plating bath. Isotopic exchange would result in the presence of both active trivalent and active hexavalent chromium in a given plating bath, regardless of which was added, and might thereby invalidate any conclusion regarding which ion yielded the chromium deposit.

The isotopic exchange was studied with a stock solution containing approximately 260 g/l of chromic acid anhydride and potassium chromic sulfate equivalent to a trivalent chromium concentration of 13 g/l. The ratio of Cr^{VI}/Cr^{III} was approximately 10. To one portion of this solution, active chromic acid was added, and to the other, active chromic chloride. These solutions were kept at 50 C, and at appropriate intervals 5 ml samples were pipetted into a lead nitrate solution. The precipitated lead chromate was filtered off, washed, dissolved in an acid solution of hydrogen peroxide, and evaporated to about 10 ml. The filtrate and washings containing the trivalent chromium were collected and also evaporated to about 10 ml. The two solutions were then transferred to test tubes, diluted to equal volumes, and their respective activities were measured.

Table I summarizes the results obtained. The fourth and fifth columns indicate the activity in counts per second of the trivalent and hexavalent chromium fractions, while the sixth column indicates the activity of a 5 ml sample of the original solution. The difference between this latter value and the sum of the activities of the two fractions indicates the approximate accuracy of the procedure. The seventh column indicates the percentage of the tracer originally present that has undergone isotopic exchange.

These data indicate that in 1 hour in this bath, the isotopic exchange would be of the order of 0.5 per cent for the hexavalent tracer or 4 per cent for the trivalent tracer. The last sample referred to in Table I contained active trivalent chromium and was heated 3 hours in the steam bath. The

90 per cent exchange obtained in this experiment agrees closely with the equilibrium value that would be expected, since about 92 per cent of the chromium in this bath was hexavalent chromium.

ELECTRODEPOSITION

The chromium plating bath used for these experiments was similar to that used commercially except that it had a higher concentration of trivalent chromium than is usually present. The bath contained 250 g/l of chromic acid, CrO_3 (equivalent to 130 g/l of hexavalent chromium), 2.5 g/l of sulfuric acid, and 12 g/l of trivalent chromium. Since trivalent chromium can exist in several different modifications which might influence the course of the plating, it was introduced into the chromic acid bath by two different methods. In three baths, it was produced by electrolytic reduction directly in the chromium plating bath. In one bath, it was introduced into the chromic acid solution in the form of the hydrated chromic oxide, which was

TABLE I. *Isotopic exchange of* Cr^{51} *between* Cr^{III} *and* Cr^{VI}

Tracer added as	Temp C	Time hours	Activity in counts/sec			Exchange
			Cr^{III}	Cr^{VI}	Original bath	
						%
Cr^{III}	50	0.25	18.8	0.99	20.2	5
		21	19.8	0.48	20.2	2
		314	7.5	9	—	55
Cr^{VI}	50	0.25	0.13	20	19.7	0.7
		3	0.05	—	19.7	0.3
		25	0.09	—	18	0.5
		315	0.86	14.9	—	5.5
Cr^{III}	90	3	1.85	—	17.7	90

prepared by precipitation with ammonium hydroxide from a solution of chromic chloride, followed by repeated decantation until the water was chloride-free. The tracer was added as either CrO_3 or $CrCl_3$, prepared as above.

The plating baths were operated at approximately 50 C, with cathode efficiencies between 15 and 22 per cent.

The cathodes were brass tubes 10 cm (4 inches) long, 2.5 cm (1 inch) in outside diameter, and had a wall thickness of 0.16 cm ($\frac{1}{16}$ inch). During the plating operation, the ends of the tubes were closed with rubber stoppers and the electrical connections were made to the inside of the tubes. The tubes were held in a vertical position inside a cylindrical porous cell which was contained in a liter beaker. The anode was a concentric cylindrical sheet of lead that fitted the inside wall of the beaker. About 800 ml of the plating solution were used, with approximately half of it inside the porous cell. The chromium was deposited at about 30 amp/dm² for 5 to 7 minute intervals, and the weight of the deposit was determined by weighing the cathode before and after plating.

The porous cell prevented anodic oxidation of trivalent chromium during the electrolysis. In order to keep isotopic exchange at a mimimum, the

three deposits (on separate cathodes) from each bath were completed within one hour after adding the tracer.

Measurements of the gamma-ray activity of the deposit were made by inserting the counter into the brass tube and counting for 30 minutes. The tube was then rotated 180° and the activity was counted for another 30 minutes. A background count was made with a brass tube for the same period of 1 hour and was subtracted from the count of the plated tube. The data for the 5 baths used are given in Table II.

TABLE II. *Results of electrodeposition experiments*

Bath	Initial chromium content			Tracer		R (tracer) / (inactive chromium)	Weight grams	Deposit activity counts per sec	Specific activity counts per sec	$*e^{-\lambda t}$	**Corrected specific activity counts per sec	Age of bath minutes
	Cr^{VI} g/l	Cr^{III} Source	Cr^{III} g/l	g/l	Valence as added							
1	137		0	0.1526	VI	1.11×10^{-3}	0.129	2.39	18.5			
							0.148	2.68	18.1			
							0.169	2.93	17.4			
									Average 18.0	1.00	18.0	
2	130	Hydrated chromic oxide	10	0.1713	VI	1.32×10^{-3}	0.172	3.41	19.9			
							0.154	3.13	20.4			
							0.151	3.03	20.1			
									Average 20.1	0.97	17.5	
3	135	Electrolytic	12	0.0253	III	2.11×10^{-3}	0.098	−0.01				
							0.128	0.01				
							0.102	−0.01				
									Average 0.0		0.9	
4	135	Electrolytic	12	0.1285	VI	0.95×10^{-3}	0.190	2.13	11.2			
							0.143	1.65	11.5			
							0.162	1.91	11.8			
									Average 11.5	0.81	16.6	
5	135	Electrolytic	12	0.1863	III	1.38×10^{-3}	0.174	0.15	0.85	0.69	0.99	0-6
							0.150	0.33	2.20		7.56	6-12
							0.146	1.63	11.1		12.9	72-78
							0.153	1.97	12.9		15.0	138-144

* $e^{-\lambda t}$ = decay factor, $\lambda = 0.0262$/day = disintegration constant of Cr^{51}, t = time in days.

** Corrected specific activity = $\frac{\text{specific activity}}{e^{-\lambda t}} \times \frac{R_1}{R_n}$

Since the half-life of the radioactive chromium was 26.5 days and the measurements of radioactivity were made over a period of two weeks, it was necessary to correct the later measurements for the natural decay of the active chromium in order to put all the results on a comparable basis. This was done by dividing the specific activity (counts per sec per gram) by the factor $e^{-\lambda t}$ (which is given in column 11 of the table) where t is the time in days elapsed since the first activity measurement, and $\lambda = 0.0262$/day is the disintegration constant of Cr^{51}.

The specific activities of the deposits must be adjusted further in order to put them on a comparable basis, because the baths from which they were deposited were not of the same activity. In these experiments, it would

have been desirable to have the ratio, R, of radioactive tracer to the inactive chromium (in a given valence state) the same for all the baths, but this was not convenient. To make the deposits from different baths comparable, their activities were corrected to the value which would have been obtained had they all been plated from baths having the same value of R as bath 1, namely 1.11×10^{-3}. This was done by multiplying the specific activities by R_1/R_n, as was done in column 7.

Bath 1 contained no trivalent chromium, and the tracer was added as CrO_3. The activity of the deposit from this bath is a standard with which to compare other deposits.

Bath 2 was like bath 1 except that precipitated chromium oxide had been dissolved in it. The average activity of the deposits from this bath agreed with that of bath 1 within the reproducibility of the measurements. This indicates that only the chromium originally present in the hexavalent state was electrodeposited. If any of the trivalent chromium had been plated out, the activity of the deposit would have been less.

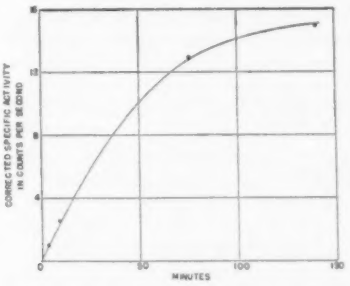

FIG. 1. Increase of activity of chromium deposits resulting from progressive oxidation of radioactive Ce^{III} in plating bath 5.

Bath 3 was prepared by the electrolytic reduction of chromic acid and addition of active trivalent chromium. The activities of the deposits were too low to determine. This indicates that the chromium originally present in the trivalent state did not plate out.

Bath 4 was prepared by electrolytic reduction of chromic acid and addition of active hexavalent chromium. The average activity of the deposits from this bath was virtually the same as for baths 1 and 2.

Bath 5 was prepared like bath 3 except that a larger amount of active chromium was used, and it was operated without the porous cell. The additional concentration of tracer makes the measurements more sensitive to small amounts of trivalent chromium that might plate out. The bath was operated for a total time of 144 minutes. The deposits were made during the periods indicated in the table. In Fig. 1 the activities of the deposits are plotted against the age of the bath. As would be expected, in the absence of a porous cell the activity of the deposits approached that of bath 1 as anodic oxidation of trivalent to hexavalent chromium proceeded. This curve can be extrapolated to zero activity at zero time and thus confirms the results of bath 3. In the calculation for these deposits, R was computed

by dividing the weight of the active chromium by the weight of the total chromium in the bath.

Immediately after the final deposits were made from baths 2 and 3, samples were taken for isotopic exchange determinations. It was found that bath 2 had undergone a 1 per cent exchange and bath 3 a 4 per cent exchange. The effects of these exchanges on the activities of the deposits were too small to be detected by the procedures used.

CONCLUSIONS

The results of these experiments show that the chromium originally present in the bath in the hexavalent state is electrodeposited, and that the chromium originally present in the trivalent form is not. They thereby confirm the theory that chromium metal is deposited directly from the hexavalent chromium present in the bath.

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Any discussion of this paper will appear in the discussion section of Volume 96 of the TRANSACTIONS of the Society.

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THE ELECTROLYTIC REDUCTION OF MALEIC ACID TO SUCCINIC ACID IN ACID SOLUTION[1]

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ABSTRACT

The electrolytic reduction of maleic acid in solutions of sulfuric acid has been studied at cathodes of copper, zinc, cadmium, mercury, aluminum, tin, lead, bismuth, iron, cobalt, and nickel. The best yield of succinic acid was obtained at a mercury cathode. The activities of copper and nickel cathodes were affected by etching. Changes in the physical structures of other cathodes, with the possible exception of zinc, were transient in effect.

INTRODUCTION

The study of the relationship between the cathode and the products of the electrolytic reduction of organic compounds has been extended in this communication to include carbon-carbon double bonds as exemplified by maleic acid. Although maleic acid may be reduced in both acid and alkaline solution, the present study was limited to solutions of sulfuric acid.

The first work on the electrolytic reduction of maleic acid in acid solution seems to have been carried out by Pomilio (1) who found that reduction took place at a spongy nickel cathode in both alcoholic and aqueous solutions of sulfuric acid. Later Norris and Cummings (2, 3) obtained over 90 per cent yields of succinic acid at a lead cathode in sulfuric acid solution. In the preamble to their patent (2), they state that iron, copper, graphite, carbon, tin, zinc, and mercury electrodes may be used. In patents taken out by Yabuta and Zaidan Hojin Rikagaku Kenkyujo (4) there is mentioned the reduction of maleic acid to succinic acid at a lead cathode in sulfuric acid solution. The reduction of maleic acid to succinic acid in a solution of benzenesulfonic acid is described by Kyrides and Bertsch (5).

The reduction of maleic acid at the dropping mercury cathode in hydrochloric acid solution has been studied by Herasymenko and Tyvońuk (6), Gosman and Heyrovský (7), Schwaer (8), Heyrovský, Smoleř, and Šťastný (9), Vopička (10), Semerano and Bettinelli (11, 12), and Herasymenko (13).

EXPERIMENTAL PROCEDURE AND RESULTS

The general procedure has been described in a chapter of a previous publication from this laboratory and references therein by one of the authors (14).

The procedure for the recovery of succinic acid was based on that of Norris and Cummings (3). In the first part of the investigation, the catholyte was poured into a beaker and allowed to evaporate on a hot plate until

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its volume was 50 cm^3. The beaker was then placed in an ice bath until crystallization was complete. The crystals were filtered through a sintered glass crucible and recrystallized from water until they melted at 179 C or slightly higher. In the later experiments with active cathodes, the catholyte in the beaker was cooled, without evaporation to 0 C and the crystals filtered off. The filtrate was then allowed to evaporate to small volume, cooled again to 0 C, and a second crop of crystals, always less than one gram, filtered off. The first crop only was purified in the usual manner, but the yield was the combined weight of both crops of crystals.

The results of a general survey of the behavior of cathodes are shown in Table I.

DISCUSSION OF RESULTS

It may be seen that mercury was by far the best cathode at both temperature ranges and it is interesting to note that the effect of increase of temperature on its activity is comparatively small.

The two poorest cathodes were bismuth and cobalt. The low yields at cobalt are partially attributable to difficulty in purifying the product. It is again interesting to note that an increase in temperature had little effect on the yields at these cathodes.

In the majority of cases increasing the temperature increased the yield markedly.

Due to the losses in recovering such small amounts of product, the inability of the authors to duplicate the 90 per cent yields of Norris and Cummings (2, 3) at lead cathodes is understandable. With the exception of copper and nickel cathodes and possibly of zinc, no consistent difference in yield attributable to the physical structures of the cathodes was found. An etched copper cathode was less active than one of smooth copper while the reverse was true of nickel. The activity of an etched nickel cathode at room temperature was unusual. Runs 119, 120, and 121 were carried out after those at the higher temperatures. It is possible that the structure of the cathode had changed after so many anodizations and runs (14).

Studies of the effect of the concentration of sulfuric acid, the current density, and the duration of the reaction were carried out at cathodes of cadmium cast at 270 C, tin cast at 70 C, electroplated lead, and etched nickel in an attempt to improve the yield. The increases in yield were negligible. It was found, however, that the conditions of sulfuric acid concentration, current density, and temperature described in Table I were optimum for these cathodes. The yields of runs extending over long periods were more or less inconsistent probably due to etching of the cathode surface which would be expected in the presence of organic acids (15).

SUMMARY

The electrolytic reduction of maleic acid to succinic acid has been studied in acid solution at cathodes of copper, zinc, cadmium, mercury, aluminum, lead, tin, bismuth, iron, cobalt, and nickel.

The highest yield of succinic acid was obtained at a mercury cathode and the lowest at bismuth and cobalt cathodes.

The effects of changes in physical structure of the cathodes on the yields were inconclusive with the exception of those in copper and nickel, and possibly those in zinc cathodes.

TABLE I. *Electrolytic reduction of maleic acid to succinic acid*

Influence of temperature

Anode: lead.
Anolyte: 10 per cent sulfuric acid.
Cathode area: 100 cm².
Current density: 0.05 amp/cm²; total current: 5 amp.
Catholyte: 95–122 cm³ of 30 per cent sulfuric acid containing 10 grams of maleic acid.
Duration of run: 55 minutes (theoretical).

Run No.	Cathode*	Temp C	Grams of succinic acid	Per cent current and material yield of succinic acid
1	Copper	28–30	1.85	18†
2	Copper	28–30	1.4	13.6
3	Copper	28–30	2.2	21.4
4	Copper etched	28–30	1.7	16.5
5	Copper etched	28–30	1.4	13.6
6	Copper	65–70	6.5	63.2†
7	Copper	65–70	5.6	54.7
8	Copper	65–70	5.2	50.6
9	Copper etched	65–70	4.2	40.9
10	Copper etched	65–70	3.9	38
11	Zinc No. 1	28–30	2.8	27.4
12	Zinc No. 1	28–30	2.5	24.4
13	Zinc No. 1	28–30	1.7	16.5
14	Zinc No. 1	28–30	2.2	21.4
15	Zinc No. 1	65–70	6.8	66.2
16	Zinc No. 1	65–70	7.6	74
17	Zinc No. 1	65–70	7.6	74
18	Zinc No. 1	65–70	7.4	72
19	Zinc No. 3 Set 1	65–70	5.3	51.6
20	Zinc No. 3 Set 1	65–70	5.0	48.7
21	Zinc No. 3 Set 2	65–70	5.0	48 7
22	Zinc No. 3 Set 2	65–70	5.4	52.6
23	Cadmium No. 4	28–30	3.0	29.2
24	Cadmium No. 4	28–30	2.4	23.4
25	Cadmium No. 9	28–30	2.0	19.5
26	Cadmium No. 9	28–30	2.7	26.3
27	Cadmium No. 8	28–30	1.7	16.5
28	Cadmium No. 8	28–30	1.5	14.6
29	Cadmium No. 4	65–70	7.5	73
30	Cadmium No. 4	65–70	7.2	70.1
31	Cadmium No. 4	65–70	7.1	69.1
32	Cadmium No. 4	65–70	7.5	73
33	Cadmium No. 9	65–70	5.8	56.5
34	Cadmium No. 9	65–70	6.6	64.3
35	Cadmium No. 8	65–70	5.0	48.7
36	Cadmium No. 8	65–70	5.4	52.6
37	Cadmium No. 8	65–70	6.8	66.2
38	Cadmium No. 8 Set 1	65–70	7.3	71
39	Cadmium No. 8 Set 2	65–70	7.1	69.1
40	Cadmium No. 8 Set 2	65–70	7.3	71

At most cathodes, the yields of succinic acid increased markedly with the temperature.

TABLE I.—*Continued*

Run No.	Cathode*	Temp C	Grams of succinic acid	Per cent current and material yield of succinic acid
41	Cadmium No. 8 Set 3	65–70	7.2	70.1
42	Cadmium No. 8 Set 3	65–70	7.5	73
43	Mercury‡	28–30	8.9	86.7
44	Mercury‡	28–30	8.8	85.6
45	Mercury‡	65–70	9.8	95.4
46	Mercury‡	65–70	10.4	100.1
47	Aluminum	28–30	1.7	16.5
48	Aluminum	28–30	1.3	12.7
49	Aluminum	65–70	4.6	44.6
50	Aluminum	65–70	6.1	59.4
51	Tin No. 16	28–30	1.1	10.7
52	Tin No. 16	28–30	1.7	16.5
53	Tin No. 16	65–70	6.9	67.2
54	Tin No. 16	65–70	7.2	70.1
55	Tin No. 18 Set 1	65–70	7.1	69.1
56	Tin No. 18 Set 1	65–70	7.1	69.1
57	Tin No. 18 Set 2	65–70	7.5	73
58	Tin No. 18 Set 2	65–70	7.8	76
59	Tin No. 20	28–30	2.8	27.4
60	Tin No. 20	28–30	2.7	26.3
61	Tin No 20	65–70	5.7	55.5
62	Tin No. 20	65–70	6.0	58.4
63	Tin No. 20	65–70	6.8	66.2
64	Tin No. 20	65–70	6.9	67.2
65	Tin No. 20	65–70	7.5	73
66	Tin No. 20	65–70	7.5	73
67	Lead	28–30	3.6	35
68	Lead	28–30	3.1	30.3
69	Lead	65–70	7.6	74
70	Lead	65–70	7.3	71
71	Lead	65–70	8.0	77.8
72	Lead	65–70	7.8	76
73	Lead No. 12	28–30	3.0	29.2
74	Lead No. 12	28–30	3.7	36
75	Lead No. 12	65–70	7.2	70.1
76	Lead No. 12	65–70	6.8	66.2
77	Lead No. 12 Set 1	65–70	4.0	38.9
78	Lead No. 12 Set 1	65–70	4.5	43.8
79	Lead No. 12 Set 2	65–70	6.9	67.2
80	Lead No. 12 Set 2	65–70	6.3	61.3
81	Lead No. 13	28–30	2.0	19.5
82	Lead No. 13	28–30	1.8	17.5
83	Lead No. 13	65–70	6.3	61.3
84	Lead No. 13	65–70	6.6	64.3
85	Lead No. 13	65–70	6.6	64 3
86	Lead No. 13	65–70	7.1	69.1
87	Lead No. 13	65–70	7.6	74
88	Lead No. 13	65–70	6.8	66.2
89	Lead No. 13 Set 1	65–70	6.7	65.2
90	Lead No. 13 Set 1	65–70	7.8	76

TABLE I.—*Concluded*

Run No.	Cathode*	Temp C	Grams of succinic acid	Per cent current and material yield of succinic acid
91	Lead No. 13 Set 1	65–70	7.6	74
92	Lead No. 13 Set 2	65–70	5.2	50.6
93	Lead No. 13 Set 2	65–70	6.2	60.4
94	Lead plate	65–70	7.7	75
95	Lead plate	65–70	7.3	71
96	Lead plate	65–70	7.6	74
97	Lead plate	65–70	7.3	71
98	Lead plate	65–70	7.0	68.2
99	Lead plate	65–70	7.5	73
100	Bismuth plate	28–30	1.9	18.5
101	Bismuth plate	28–30	3.0	29.2
102	Bismuth plate	65–70	3.8	37
103	Bismuth plate	65–70	3.3	32.1
104	Iron	28–30	3.6	35
105	Iron	65–70	7.4	72
106	Iron	65–70	7.1	72
107	Iron	65–70	6.0	58.4
108	Cobalt plate	28–30	2.7	26.3
109	Cobalt plate	28–30	2.8	27.4
110	Cobalt plate	65–70	3.0	29.2
111	Cobalt plate	65–70	3.0	29.2
112	Nickel	28–30	3.0	29.2
113	Nickel	28–30	3.0	32.1
114	Nickel	28–30	2.6	25.3
115	Nickel	28–30	3.5	34.2
116	Nickel (Etched)	28–30	1.9	18.5
117	Nickel (Etched)	28–30	2.6	25.3
118	Nickel (Etched)	28–30	2.3	22.4
119	Nickel (Etched)	28–30	2.2	21.4
120	Nickel (Etched)	28–30	5.5	53.8
121	Nickel (Etched)	28–30	6.6	64.3
122	Nickel (Unetched)	65–70	6.3	61.3
123	Nickel (Etched)	65–70	7.6	74
124	Nickel (Etched)	65–70	7.6	74
125	Nickel (Etched)	65–70	7.6	74
126	Nickel (Etched)	65–70	7.8	76
127	Nickel (Etched)	65–70	7.1	69.1

‡ Platinum anode.

† Average of several runs.

* Definitions:

Copper—etched with nitric acid.
Zinc No. 1—cast at 370 C.
Zinc No. 3—cast at room temperature.
Cadmium No. 4—cast at room temperature.
Cadmium No. 9—cast at 270 C. Machined and etched in 98% chromic acid and 2% nitric acid.
Cadmium No. 8—cast at 270 C.
Tin No. 16—cast at room temperature.
Tin No. 18—cast at 180 C.
Tin No. 20—cast 70 C.
Lead No. 12—cast at 270 C.
Lead No. 13—cast at room temperature.
Lead plate—electroplated from a perchlorate bath.
Bismuth plate—electroplated from a perchlorate bath.
Cobalt plate—electroplated from a sulfate bath.
Nickel etched—with nitric acid.

ACKNOWLEDGMENTS

In addition to those made in a previous paper, the authors would like to make additional acknowledgments. Electrodes were cast by V. B. Utzinger. Lead was electroplated by R. J. Mauterer. The authors would like to express their appreciation to J. R. Musgrave of the Eagle Picher Company for the lead. The advice of W. M. Langdon of the Division of Chemical Engineering and of N. J. Leonard of the Division of Organic Chemistry in the early stages of the work is gratefully acknowledged.

Any discussion of this paper will appear in the discussion section of Volume 96 of the TRANSACTIONS of the Society.

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PREPARATION OF HYPER-PURE SILICON[1]

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ABSTRACT

The preparation of hyper-pure silicon by reduction of silicon tetrachloride with zinc vapor is described. This reaction, which takes place at 950 C, was carried out in apparatus constructed of fused silica. The silicon prepared by this process was essentially spectrographically free of metallic impurities, and had extremely low electrical conductivity.

INTRODUCTION

Becket (1) is usually credited with the first successful attempt to prepare high-purity silicon, and a somewhat similar procedure was developed by Tucker (2). A brief but critical review of the literature up to 1933 is presented by Greiner, Marsh, and Stoughton (3). Since that date, the principal advances have been the synthesis of pure silicon on a very small scale by the hot wire process of van Arkel (4), and purification of 99.8 per cent silicon by the melting technique of Scaff (5).

At the outbreak of World War II, the only available silicon of high purity was obtained by leaching commercial silicon. The process described in this paper was developed for the production of extremely pure silicon which was used in crystal rectifiers because of its semiconducting properties.

EXPERIMENTAL

Elemental silicon can be derived from silicon tetrachloride by reduction with active metals such as magnesium, aluminum, and zinc. However, the choice of reductant must be made with other considerations in mind; namely, (*a*) purity and cost, (*b*) formation of silicides, (*c*) reactivity with container material, and (*d*) ease of removal of by-products and excess reagent. Zinc satisfies each of these criteria remarkably well, and after initial experimentation, the reaction between zinc and silicon tetrachloride was chosen for larger scale production. Zinc is sufficiently reactive to remove chlorine from silicon tetrachloride and yet it will not attack fused silica containers.

Raw materials

The zinc used was of 99.99 per cent purity, and was purchased from a commercial producer in 45-pound (22.7-kg) slabs. These were cut into small pieces approximately three by one and one-half inches (7.6 by 3.8 cm) in size. Cleaning was accomplished by allowing the zinc to stand for 20–30 minutes in 20 per cent hydrochloric acid, removing any loose dirt, rinsing with water, and drying.

Silicon tetrachloride of cp grade was purchased and redistilled. It should be noted that the silicon produced from this material probably contained

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very small amounts of carbon. This could be prevented, if desired, by a suitable method of removing carbon from the starting material.

A special grade of oil-pumped dry nitrogen of very low oxygen content was used in all cases without further purification.

Apparatus

The apparatus used in this synthesis was composed almost entirely of fused silica, and is shown in Fig. 1. The reactor (R) was a tube eight inches (20 cm) in diameter and six feet (1.83 m) long. The collector (K) was twelve inches (30 cm) in diameter and twenty-four inches (61 cm) high. The reactor, collector, zinc traps, baffles, preheater, end plate, and exit tube were all made of opaque silica. The zinc boilers (Z, Z) of one-liter capacity and the silicon tetrachloride vaporizer (S, 250 ml) were transparent silica. The lid (L) of the collector was fabricated from one-inch (2.5 cm) transite, and the plug (P) was a cork stopper coated with asbestos paper. Where it was necessary to join one piece to another, and welding was not feasible, seals were made with the best grade of asbestos.

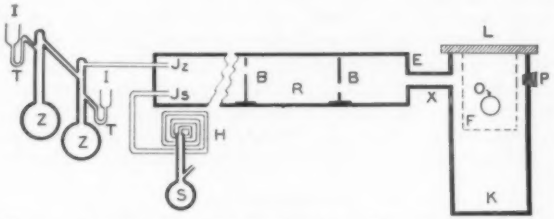

FIG. 1. Apparatus for the preparation of hyper-pure silicon

The heating system consisted of seven separately controlled units, for (1) the silicon tetrachloride vaporizer, (2) and (3) zinc traps, (4) and (5) the zinc boilers, (6) the main reactor, and (7) the connecting tube between the exit of the reactor and the large collector. The main reactor was heated by globars, while all the other furnaces were gas-fired. In addition, an auxiliary furnace served for melting the zinc, which was placed in silica crucibles.

Thermocouples with suitable recording devices were situated in each heating unit. These are not shown in the diagram in order to prevent the inclusion of too many items in a limited space. In every instance, these consisted of "chromel-alumel" elements enclosed in silica protection tubes; in the case of the main reactor, two thermocouples were placed outside of the reaction tube (R).

The housing for all the furnaces was constructed of K-23 or Na-23 firebrick; this is not shown in the diagram.

Operation

The entire apparatus was dried thoroughly and then swept out for at least two hours with dry nitrogen, during which time the globars surrounding the main reactor were permitted to heat up to about 500 C, at which time the auxiliary furnaces were turned on. When the temperature of the traps reached 550 C and that of the boilers 700 C, zinc was melted and

poured (after removing the dross) into the boilers (Z, Z) through the inlet tubes (I, I). The latter were covered with silica plates having a hole in the center, through which passed a silica tube; nitrogen was admitted through these in order to prevent oxidation of the zinc. The various furnaces were then raised to the following temperatures:

Main reactor	950 C
Traps	550 C
Zinc boilers	700–750 C
Silicon tetrachloride vaporizer	625–675 C
Exit tube	1000–1025 C

When the above temperatures had been reached, the zinc boilers were raised to 980 C. As soon as the zinc began to boil, silicon tetrachloride was introduced into the vaporizer (S) which was half-filled with chips of silica; from there it passed through the preheater (H), and into the reactor (R) at the jet (Js). The zinc boiled into the reaction zone through the adjacent opening (Jz). Operation occurred more smoothly when baffles (B, B) were placed about ten inches (25 cm) and thirty-six inches (91 cm) from the exit end of the reactor. Unreacted zinc and silicon tetrachloride, together with zinc chloride, passed through the exit tube (X) into a large collector (K), which also contained a transite baffle (F). Silicon tetrachloride passed through opening (O) to a condensing system, while zinc and zinc chloride collected in (K). In order to prevent plugging, the exit tube was cleaned periodically by inserting a silica rod through the opening closed by plug (P), and moving the rod back and forth through (X).

Whenever the level in either zinc boiler dropped to about one-quarter full, more zinc was added, and at the same time the other boiler was raised to a higher temperature in order to maintain a constant vaporization rate.

During normal operation, a slight excess of silicon tetrachloride was present. This was checked by observing the silicon tetrachloride condenser.

About 15–16 pounds (7 kg) of silicon were produced per run, during which time approximately 145–150 pounds (65–68 kg) of zinc were used [five pounds (2.25 kg) per hour] with an equivalent quantity [about 190 pounds (86 kg)] of silicon tetrachloride. The reaction, therefore, required about 30 hours' time.

When the reaction was terminated, all the zinc in the boilers was vaporized, zinc in the traps was blown into the boilers by a stream of nitrogen, and then this zinc was boiled out. The boiler, trap, and exit furnaces were shut off, and the reactor power supply was turned off. Nitrogen was passed through the zinc boiler systems. Silicon tetrachloride was fed into the reactor until the temperature of the latter had dropped to 750 C, at which time the silicon tetrachloride was shut off, and nitrogen passed through in its place. The vaporizer furnace was then turned off. When the reactor had cooled to 150 C, the collector was disconnected, and the reactor opened. The reactor was nearly completely filled with crystalline silicon.

Purification

By inspection, any pieces of silica, scales, or asbestos were removed. The remainder of the product was placed in a large porcelain mortar, where large crystal masses were crushed. Five pound (2.25 kg) portions were then digested overnight in six-liter Erlenmeyer flasks with concentrated hydrochloric acid, in order to remove iron and any other acid-soluble metals.

This mixture was then diluted with water, and digested for four hours at 100 C. After diluting, the product was filtered on a Buchner funnel, washed with water, transferred to glass trays, and dried at 100 C. The dried silicon was then transferred to platinum-clad dishes, and digested with a sulfuric-hydrofluoric acid mixture (to dissolve silica) until fumes of sulfur trioxide were evolved. After cooling, the contents of the dishes were transferred to beakers containing distilled water, filtered, washed, and again dried at 100 C.

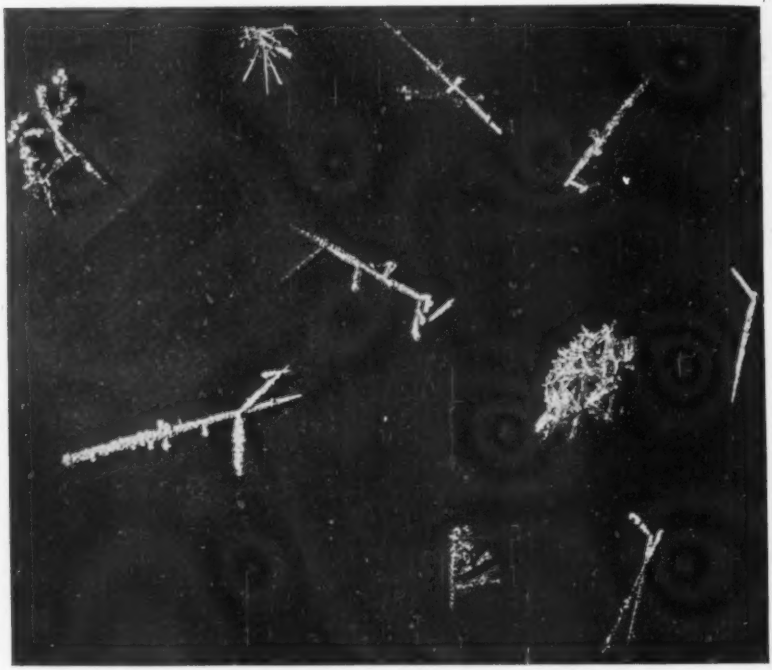

FIG. 2. Silicon crystals (one-half actual size)

Properties

The purified silicon consisted of metallic gray crystals, which were practically spectrographically free of foreign metals; the metallic impurity content was not over 0.001 per cent. However, as mentioned previously, the silicon sometimes contained small amounts of carbon (about 0.03 per cent). The element was thus about 99.97 per cent pure.

Measurements by Professor Karl Lark-Horovitz of Purdue University on a needle of silicon about 0.25 mm in diameter and 10 mm long indicated that the sample was a single crystal.

At 25 C, silicon needles had a conductivity of 0.01 reciprocal ohm-centimeter, according to data obtained by Professor Frederick Seitz at the Carnegie Institute of Technology. Other electrical properties of hyper-pure silicon are given by Pearson and Bardeen (7).

Photographs of some typical silicon crystals are shown in Fig. 2.

Uses

The high-purity silicon prepared by the above process was used as the semiconductor element in crystal rectifiers. A complete description of this subject is given by Torrey and Whitmer (6).

DISCUSSION OF RESULTS

The process described is the first in which pure silicon was prepared directly, without a series of lengthy acid leachings. As a matter of fact, the product before purification was of extremely high purity, and hydrochloric and hydrofluoric acid treatments were employed primarily because it had been necessary to standardize the procedure early in the work. When production difficulties were eliminated, it was shown in many runs that the product was improved only slightly, if at all, by purification.

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REACTIONS OF ZIRCONIUM, TITANIUM, COLUMBIUM, AND TANTALUM WITH THE GASES, OXYGEN, NITROGEN, AND HYDROGEN AT ELEVATED TEMPERATURES[1]

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ABSTRACT

A systematic study is made of the kinetics of the reactions including a study of the time, temperature, and pressure variables. The reaction rates are studied by the vacuum microbalance method and the surface structures by the electron diffraction method. The data are correlated with fundamental diffusion and solution processes. Diffusion constants and energies of activation are calculated where possible and a comparison is made of the several reactions for the different metals.

INTRODUCTION

The gas phase reactions of the active metals zirconium, titanium, columbium, and tantalum are interesting both from a scientific and from a technical point of view for the following reasons: (*a*) The metals are extremely stable at room temperature to both liquid and gas phase corrosion reactions. However, at temperatures of a few hundred degrees, the metals react readily with O_2 and H_2. (*b*) The metals have high melting points and have or may have many uses in equipment operating at high temperature. (*c*) In contrast to many of the common metals, this group of metals reacts readily with nitrogen and hydrogen. A systematic study of the kinetics of such reactions has not been attempted. (*d*) The reaction products are soluble in the metal and interesting rate expressions may be observed for such systems. (*e*) The solubility of the reaction products may greatly change the physical properties of the metal. In fact many of the difficulties associated with the reduction, refining, working, and use of these metals may be due to these gas phase reactions.

A number of factors indicate that these metals may have some degree of oxidation resistance at elevated temperatures. These are: (*a*) the high melting points of the metals, (*b*) the refractory nature of several of the oxides, and (*c*) the probable formation of protective films since the volume ratio of the oxide to the metal is greater than unity. The unfavorable factors are: (*a*) the metal reacts to form nitrides and hydrides, (*b*) the oxides, nitrides, and hydrides are partially or completely soluble in the metal depending upon the temperature, and (*c*) the oxides may undergo crystal structure transformations on heating and cooling.

Therefore, it is of interest for us to study the kinetics of the gas phase reactions for the following reasons: (*a*) to establish the rate at which the metals react with the several gases and to correlate the data with funda-

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mental gas-metal rate theories, (*b*) to understand the practical difficulties of the reduction, refining, working and use of these metals, and (*c*) to understand the reactions that the metals may undergo as components in high temperature alloys.

This communication will present a brief survey of a much larger study on these reactions. It is hoped to present a more complete study of these reactions for each of the metals at a later date.

LITERATURE SURVEY

A number of papers exist in the literature on the preparation and crystal structure of the reaction products of these metals with O_2, N_2, and H_2. However, only fragmentary data exist on the kinetics of these reactions. Thermodynamic data exist for the calculation of the equilibria of the reactions of zirconium and titanium with O_2, N_2, and with C, CO, and CO_2. However, the data for columbium and tantalum are not sufficient to make a detailed analysis of the several equilibria.

Oxidation

Kinetics.—McAdam and Geil (26) have studied the rates of oxidation of a number of metals using the interference color method. Columbium is reported to oxidize faster than tantalum and slower than iron and zirconium. The oxidation of columbium has been reported by the Fansteel Metallurgical Corporation (32). Columbium starts to oxidize in air at about 200 C. The oxide is said to be adherent and prevents further reaction until the temperature is raised. The oxides of columbium are reported to dissolve in the metal when the metal is heated in vacuum between red heat and 1200 C.

Carpenter and Reavell (8) have studied the oxidation of titanium using the pressure change method at 742 and 1000 C for one-fifth of an atmosphere pressure. They have compared the observed reaction rates with what is to be expected from kinetic theory. The probabilities of reaction are calculated to be 10^{-5} for O_2 at 1000 C and 10^{-6} at 740 C.

The oxidation of zirconium at low pressures has been studied extensively. The recent work of Guldner and Wooten (20) shows that the reaction occurs at 400 C and that the oxide is formed.

Crystal structure.—The crystal structures of the oxide films formed on zirconium and titanium at temperatures of 300 to 600 C using the electron diffraction technique have been studied by Hickman and Gulbransen (23). The monoclinic form of ZrO_2 and the rutile structure of TiO_2 are observed over the complete time and temperature range. Similar studies for columbium and tantalum are being made and will be reported in another work.

The metal-oxygen constitutional diagrams for the metals together with the crystal structures and literature references are shown in Fig. 1. The Greek letters designating the phases for titanium are those of Ehrlich (13). Since the phases for the other metals have not been designated, we have extended the Greek letters to cover the additional phases for purposes of comparison. The numbers refer to the crystal structures tabulated at the side of the figure. The numbers in parenthesis refer to the literature references for the particular system. The limit of solubility of oxygen in the metal lattice has not been determined except for titanium. This is shown by the lack of definition in the boundary of the solid solution region for the other metals.

Nitrogen reaction

Kinetics.—Carpenter and Reavell (8) have reported one measurement on the reaction of pure titanium with pure nitrogen. The curve at 1000 C shows a linear dependence with time. The probability of reaction is given as 10^{-8}. The low pressure reaction of zirconium with nitrogen has been

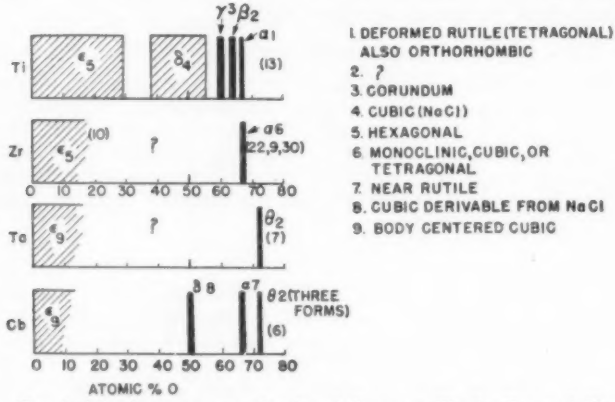

FIG. 1. Metal-oxygen constitutional diagrams Ti, Zr, Ta, and Cb

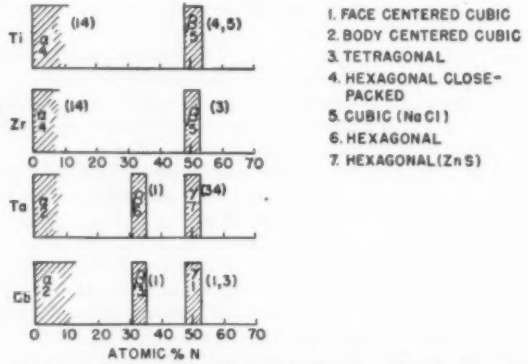

FIG. 2. Metal-nitrogen constitutional diagrams Ti, Zr, Ta, and Cb

studied by Guldner and Wooten (20). Zirconium reacts slowly at a temperature of 400 C and rapidly at 800 C to form the nitride.

Crystal structure.—The metal-nitrogen constitutional diagrams together with the crystal structures and literature references are shown in Figure 2. Again Greek letters are used to designate the phases and the numbers refer to the crystal structures found. The literature references are shown by the numbers in parenthesis.

Hydrogen reaction

Kinetics.—The reaction of zirconium with hydrogen at low pressures has been studied extensively (12, 15, 25). Guldner and Wooten (20) find that the reaction with hydrogen at low pressures occurs at a temperature of 300 C. Similar observations have been found by Ehrke and Slack (12).

Crystal structure.—An excellent review of the metal-hydrogen systems has been given by Smith (31).

The metal-hydrogen constitutional diagrams are given in Fig. 3 together with the crystal structures and literature references.

Equilibria calculations

Gulbransen and Andrew (16) have calculated the equilibria of the reactions of zirconium and titanium with oxygen, nitrogen, and carbon containing gases and the exchange reactions of H_2O and H_2 and CO_2 and CO. The calculations show for the zirconium reactions that ZrO_2, ZrN, and ZrC

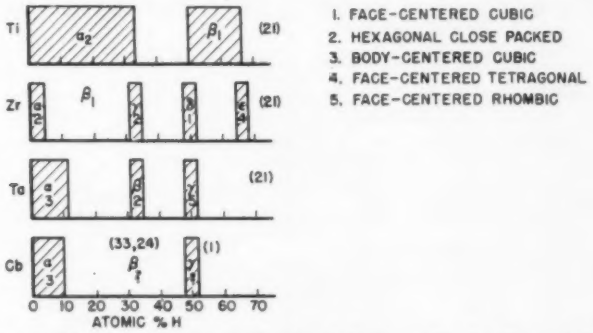

FIG. 3. Metal-hydrogen constitutional diagrams Ti, Zr, Ta, and Cb

are stable at temperatures up to 1500 C, and that zirconium will remove the gases O_2, N_2, CO, CO_2, and H_2O at 1000 C and at the lowest pressures used in modern vacuum technology. The exchange reactions of H_2O and CO_2 to form the oxide and H_2 and CO, respectively, are possible below 1100 C in vacua of the order of 10^{-7} mm of Hg.

The equilibria calculations for the titanium reactions show that TiO_2, TiN, and TiC are stable at all temperatures up to the transition point for titanium and that, from a thermodynamic point of view, titanium will remove O_2, N_2, CO, CO_2, and H_2O at 800 C at the lowest pressures used in modern vacuum technology. The exchange reactions of H_2O and carbon dioxide to form the oxide and H_2 and CO, respectively, are possible up to 800 C and perhaps higher in vacua of the order of 10^{-7} mm of Hg.

APPARATUS AND METHOD

Vacuum microbalance

The vacuum microbalance and associated equipment used in all of the kinetic measurements have been described (17, 18). The sensitivity of the

balance is 0.86 divisions per microgram and the weight change can be estimated to 0.3×10^{-6} g. The specimens weigh 0.6840 g and have surface areas of 10 to 15 cm^2.

Vacuum system and furnace tube

The vacuum system and furnace tube have been described (17, 19). The vacuum system is constructed of pyrex glass and this system is sealed directly to the double-walled zircon furnace tube. With the furnace at 900 C leak rates of 1.4×10^{-9} mm liters per second are achieved after pumping overnight. McLeod gage pressures of 10^{-6} mm or better can be achieved at temperatures of 1175 C and perhaps higher.

Gas purification

The purification of O_2 and H_2 has been described (17). N_2 is the most difficult gas to prepare free from objectionable impurities (16). The source of the N_2 is lamp grade of N_2. This is further purified before using (16).

TABLE I. *Analysis and preparation of specimens*

Metal	Analyses	Polishing procedure	Source
Cb	C 0.01 max, traces of Fe, Ti, Ta, Sn and Zr	No. 1 grit through to 4/0 paper. Last two stages under purified kerosene	Fansteel Metallurgical Corp.
Ta	C 0.03, Fe 0.01 max, Ta 99.9 +	Same	Fansteel Metallurgical Corp.
Ti	Commercial grade, C 0.77, Ti 99	Same	Remington Arms Co.
Zr	Iodide grade, Hf 3 per cent, Fe 0.04	Same	Foote Mineral Co.

Mass spectrometer analyses of the gas used for the N_2 reactions show an O_2 content of 0.01 per cent. H_2 impurities are also important, but cannot be measured effectively at these low concentrations with our mass spectrometer. An investigation of the manufacturing process for preparing the pure N_2 indicates that H_2 impurities are not be be expected.

The methods used have been described (16, 17).

Samples

The analyses of the several metal samples are shown in Table I, together with the method of preparation. The individual specimens are cut from the polished and cleaned sheet and weighed to 0.6840. The kerosene is removed by petroleum ether and the specimens are finally washed in absolute alcohol. They are stored in a desiccator prior to use.

RESULTS AND DISCUSSION

The reaction of the metals in high vacua before starting the experiment must be studied if the metal is to be maintained in an essentially film free condition. The active metals, especially zirconium and columbium, are excellent getters to the gases present in the best of high vacuum systems.

We have adopted the policy of using abraded specimens containing the

equilibrium room temperature film and then heating to the reaction temperature quickly and in the best of vacua to avoid further film formation.

The use of hydrogen to reduce the initial and vacuum formed film is impracticable for two reasons. First, the oxides of zirconium and titanium are impossible to reduce from a thermodynamic point of view. The oxides of columbium and tantalum may be reducible although precise equilibrium data are not available. Second, we have evidence for columbium and tantalum that stable hydrides may be formed at high temperatures.

Our studies show that the additional film formed on heating to the reaction temperature is less than 50 Angstroms for our worst conditions of time and temperature.

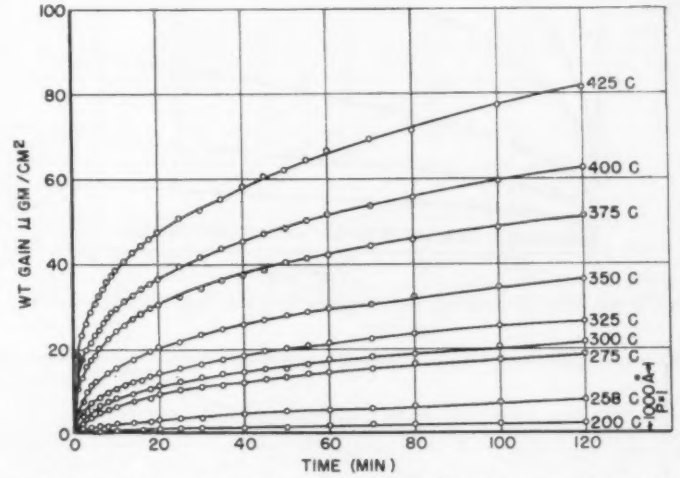

FIG. 4. Reaction of zirconium with oxygen, 7.6 cm. Effect of temperature, 200–425 C

Reaction with oxygen

The reaction is studied as a function of time, temperature, and pressure and the results are presented in Fig. 4, 5, 6, and 7. The weight gain in micrograms per cm^2 is plotted against the time in minutes. The thickness of the oxide film may be estimated if we assume the oxide to be ZrO_2, TiO_2, and CbO and that the ratio of the real to measured area is unity. A scale 1000 Å is marked on the curves. The scale is not included for tantalum since we have not determined the structure of the surface oxide to date.

The shapes of the curves are similar to those observed for other metals. A rapid reaction is first observed. This rate decreases as the film thickens. In this sense the film has protective properties. At 350 C the order of increasing rates of reaction is titanium, zirconium, tantalum, and columbium.

The parabolic rate law equation $W^2 = Kt + C$ (29, 27, 36) may be fitted to the data. In general, deviations occur in the early part of the reaction. This is to be expected from a recent prediction of Mott (28).

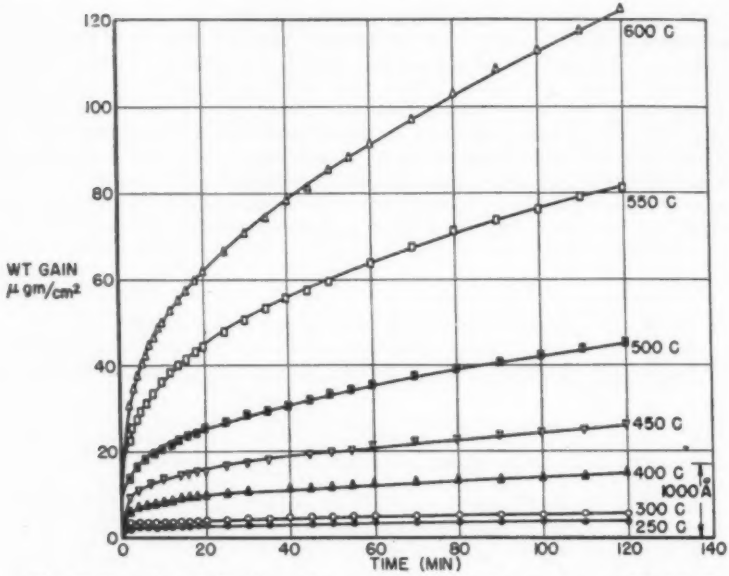

FIG. 5. Reaction of titanium with oxygen. Effect of temperature, 250–600 C

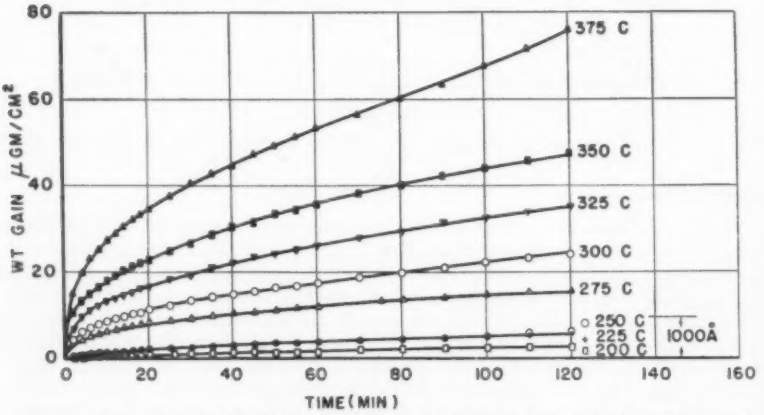

FIG. 6. Reaction of columbium with oxygen. Effect of temperature, 200–375 C, abraded samples.

The temperature dependence of the reaction is very strong. If we apply the Arrhenius equation, first used by Pilling and Bedworth (29) and later by Dunn (11), it is possible to calculate an energy of activation for the

rate governing reaction. We have done this for these reactions and from $\log K$ *vs.* $1/T$ plots we can find E, the energy of activation. K is the parabolic rate law constant. Table II shows a tabulation of these energies of activation for the four metals. The values are in line with those found for other metals.

The effect of pressure on the reaction rate will not be discussed at length here. A rather small effect is noted. This evidence supports the theory that the oxide film is the limiting barrier to reaction. Since colored films are observed and electron diffraction studies show the presence of oxides,

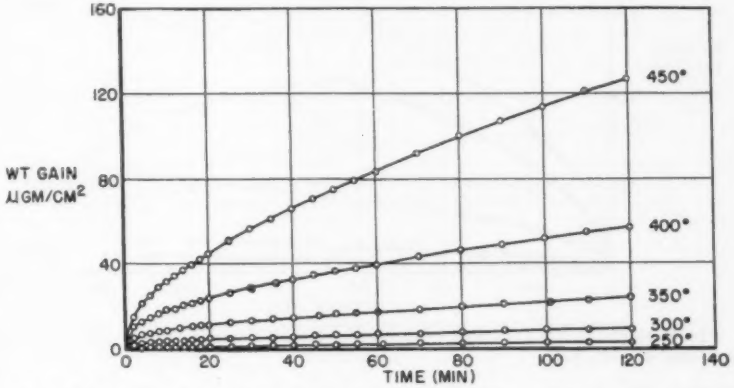

FIG. 7. Reaction of tantalum with oxygen, 7.6 cm. Effect of temperature, 250–450 C, abraded through 4/0.

TABLE II. *Energy of activation of the oxidation reactions*

Metal	Temperature range C	Energy of activation calories per mole
Cb	200–375	22,800
Ta	250–450	27,400
Ti	350–600	46,000
Zr	200–425	18,200

there appears to be little doubt that the rate of solution of the oxide is slow at the temperatures used in the oxidation studies.

Reaction with nitrogen.

The reaction is studied as a function of time, temperature, and pressure. The results are shown in Fig. 8, 9, 10, and 11. Since the nitride is partially or completely soluble in the metal, thickness calculations are not made. The weight gain is given in micrograms of nitrogen adsorbed per cm^2.

The shapes of the curves are similar to those observed for the oxidation of metals. In regard to the nitrogen reaction, the four metals fall in the following order of increasing rate of reaction: zirconium, columbium, tantalum, and titanium.

Empirically, the parabolic rate law, $W^2 = Kt + C$, may be fitted to the data. The deviations from the law occur in the early period of the reaction.

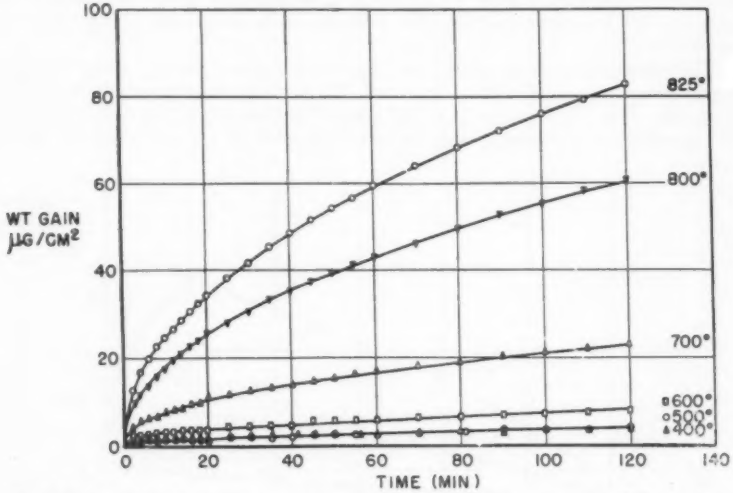

FIG. 8. Reaction of zirconium with pure nitrogen, 7.6 cm pressure. Effect of temperature, 400–825 C.

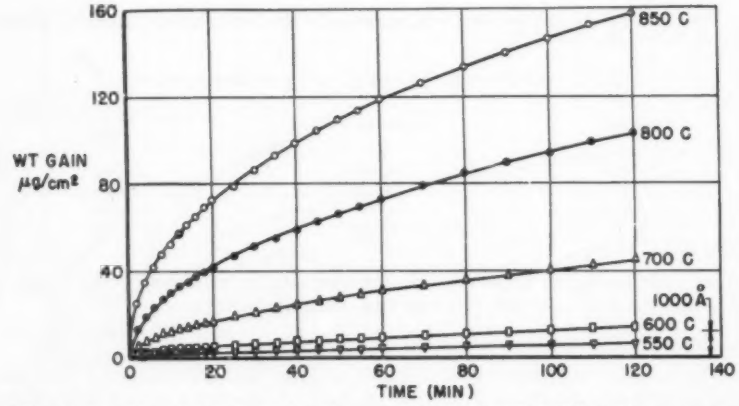

FIG. 9. Reaction of titanium with nitrogen, 7.6 cm, abraded. Effect of temperature, 550–850 C.

Colored films are not observed on the surface of the metals. The electron diffraction evidence is also negative. The evidence indicates that nitride films are not present after evacuating the system and cooling to room temperature.

A study of the effect of the gas pressure on the reaction rate shows a

very minor effect. This indicates that the reaction is not occurring on the base metal. The reaction is probably occurring through a thin, but permeable, nitride film which is dissolving into the metal at a rate approximately

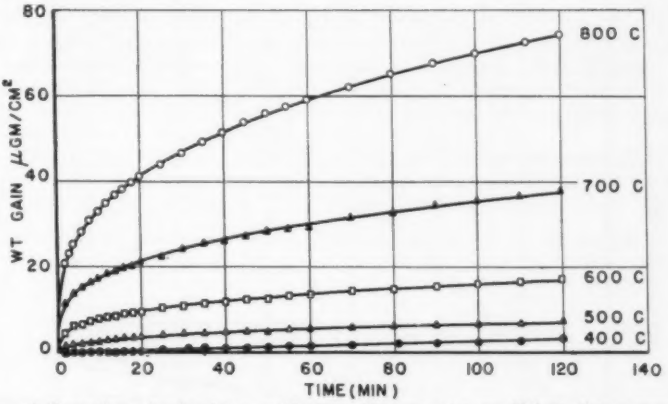

FIG. 10. Reaction of columbium with pure nitrogen, 7.6 cm. Effect of temperature, 400–800 C.

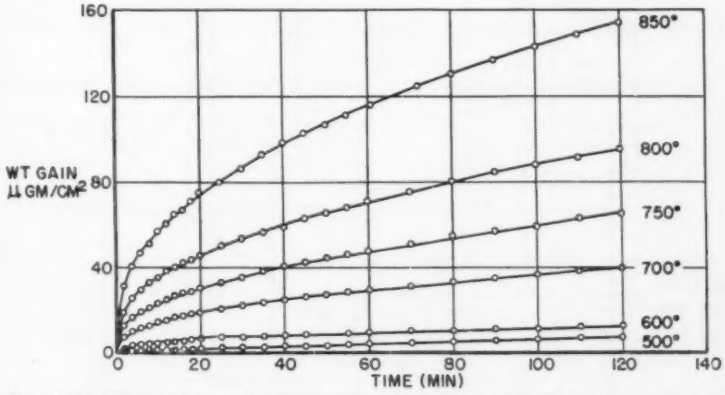

FIG. 11. Reaction of tantalum with pure nitrogen, 7.6 cm. Effect of temperature, 500–850 C, abraded through 4/0.

equal to the rate of reaction. After the nitride reaction is stopped by evacuation, the solution process continues. The nitrides are stable in all cases to temperatures of 900 to 1000 C, the highest temperatures that we have used in our tests.

Reactions with hydrogen

The reactions are studied as a function of the time, temperature, and pressure. The stability of the reaction product is studied under high vacua

conditions as a function of the temperature. The results are shown in Fig. 12, 13, and 14. The results for tantalum are not included since we have

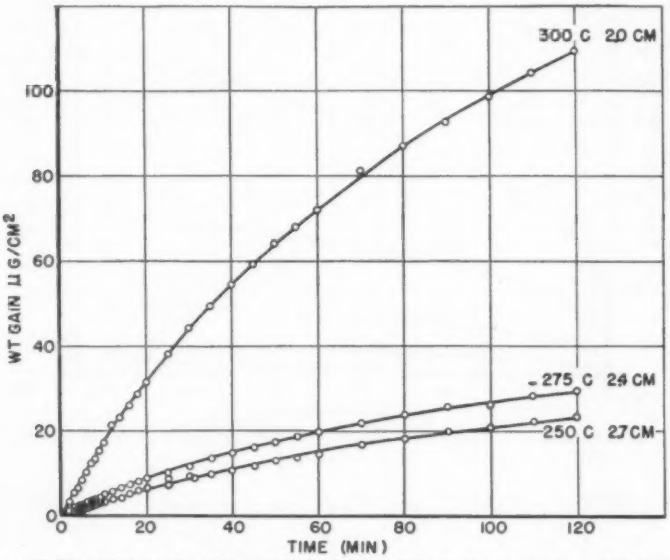

FIG. 12. Reaction of zirconium with hydrogen. Effect of temperature, 250–300 C

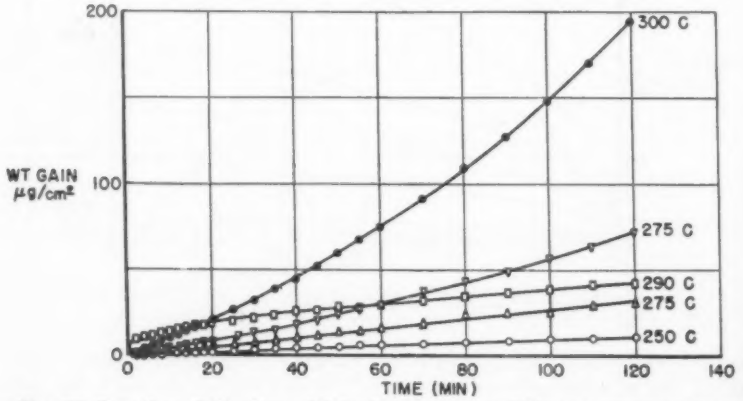

FIG. 13. Reaction of titanium with hydrogen, 2.2 cm. Effect of temperature, 250–300 C.

not been able to obtain consistent results with this metal. The hydrogen reactions are very sensitive not only to temperature, but also to surface films and impurities.

The shapes of the time curves at a given temperature are quite variable. In general, the parabolic rate law does not explain the data. The parabolic law may be derived from Van Liempt's (35) solution of the diffusion equation for a flat plate.

Barrer (2) has summarized the recent literature on the permeability of metals to gases. Two possible permeation rate-pressure relationships have been used to explain the data. These are: (*a*) the linear rate law which is based on the mechanism of activated diffusion of hydrogen without dissociation, and (*b*) the square root law which is based on the mechanism of activated diffusion with dissociation.

A study of the pressure variation of the initial reaction rate indicates that the square root of pressure relationship is followed. This indicates that the process involves solution of hydrogen in the absence of any film of hydride.

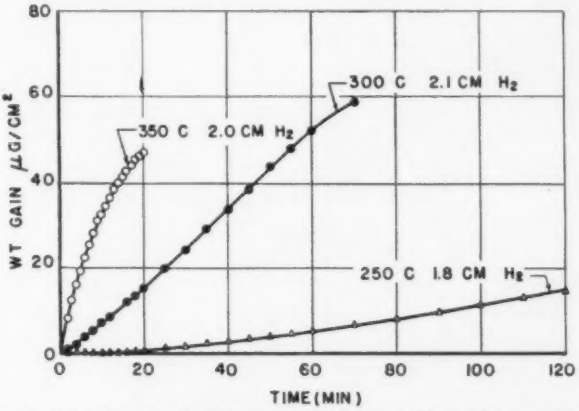

FIG. 14. Reaction of columbium with hydrogen. Effect of temperature

The data are not sufficiently consistent to calculate an energy of activation for the reaction.

The hydrides are stable in vacua up to temperatures of the order of 300 to 450 C depending upon the metal. In the cases of columbium and tantalum, stable reaction products appear to form at higher temperatures.

CONCLUSIONS

The oxidation reaction follows the parabolic law predictions although some deviations are observed during the initial period of the reactions. The rates of reaction follow an exponential function of the temperature, and energies of activation for the rate governing process are calculated. The order of increasing reactivity to oxygen at 350 C is titanium, zirconium, tantalum, and columbium.

The time behavior of the nitrogen reaction also follows the parabolic law with only minor deviations. Visual and electron diffraction evidence shows that nitride films are not present after cooling to room temperature. A study of the pressure variation of the reaction indicates only a minor

effect. A mechanism of reaction is proposed in which the rate governing mechanism is diffusion of nitrogen into the metal in the presence of a thin, but permeable, nitride film. The effect of temperature on the reaction follows an exponential relationship. The order of increasing reactivity for the nitrogen reaction at 700 C is zirconium, columbium, tantalum, and titanium.

A study of the hydride reaction indicates that low temperature stable hydrides are formed. These decompose in high vacua at temperatures between 300 and 450 C. The time behavior of the reaction rate is quite variable. No one expression fits the data. The temperature dependence is very marked while the effect of pressure indicates that the square root relation is obeyed. The reaction is thought to occur directly on the bare metal in the absence of a film, and the rate governing process is the diffusion of hydrogen atoms through the film. The order of increasing reactivity at 300 C and 2.1 cm of H_2 is columbium, zirconium, and titanium.

Any discussion of this paper will appear in the discussion section of Volume 96 of the TRANSACTIONS of the Society.

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